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METHOD OF MAKING RAPID CURING
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This invention relates to foundry products and foundry processes. In one aspect, this invention relates to a foundry process for making sand cores which can be rapidly hardened at room temperature.

In the foundry art, cores for use in making metal castings are usually prepared from mixtures of an aggregate (e.g. sand) which has been mixed with a binding amount of a polymerizable or curable binder. Such mixtures are referred to herein as "foundry mixes." The amount of binder used is typically less than 10% by weight based on the weight of the sand, e.g. from 0.5 to 5% on the same basis. Frequently, minor amounts of other materials are also included in foundry mixes, e.g. iron oxide, ground flax fibers, and the like. The binder permits a foundry mix to be molded or shaped into the desired form, usually in a pattern box or mold, and thereafter cured to form a self-supporting structure.

The time required for a freshly prepared core to reach an acceptable level of stripping strength is defined as the time that a fresh or green core must remain in a pattern box or mold to develop sufficient hardness and strength that it can be removed by foundry personnel from the pattern box or mold without destruction or substantial distortion of the core. With some binders, the cores are then completely cured or hardened by simply allowing them to dry at room temperature. With other binders, final cures must be accomplished by baking the green cores. Numerous variations of these types of final cures are known, e.g. curing at room temperature with gaseous catalysts such as CO₂.

In recent years, the foundry art has been provided with binder compositions containing both a polyisocyanate and a hydroxyl-containing reactant, with and without the presence of other ingredients. Many such binder compositions are referred to as "no-bake binders." They are capable of forming completely cured cores at room temperature without the use of gaseous catalysts. Optionally, they can be baked to accelerate the curing.

It has now been discovered that the time required for freshly prepared cores containing such binder compositions to reach an acceptable level of stripping strength can be substantially reduced by the simple addition of a metal silicate to the foundry mix. For example, one popular commercially-available binder composition contains both an aromatic poly isocyanate and an oil-modified alkyd resin. The alkyd resin has a hydroxyl value (at 100% non-volatile) in excess of 50. When this binder composition was used in the manner recommended by its manufacturer, certain sand molds prepared from foundry mixes containing this binder composition required about 45 minutes to reach an acceptable level of stripping strength. When the same sand molds were prepared in the same manner, using the same binder composition at the same concentrations, the simple addition of aqueous sodium silicate to the foundry mix reduced the stripping time to 8 minutes. Casting results obtained with the rapidly cured core were excellent.

Thus, in the ordinary practice of this invention, cores (or molds) for use in making metal castings will be prepared by the following steps:

- (1) forming a foundry mix containing an aggregate (e.g. sand) and a binder composition containing both an

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isocyanate and a hydroxyl-containing reactant, usually in conjunction with one or more catalysts:

- (2) simultaneously or preferably subsequently mixing metal silicate with the foundry mix of step 1 under hydrous conditions;
- (3) introducing the resulting foundry mix of step 2 into a mold or pattern to thereby obtain a green core (or mold);
- (4) allowing the green core to remain in the mold or pattern for a time at least sufficient for the core to attain a minimum stripping strength; and
- (5) thereafter removing the green core from the mold or pattern and allowing the core to cure, typically at room temperature.

Because of the tremendous speed with which cores prepared according to the preferred form of my invention obtain stripping strength, I prefer to add, for example, aqueous sodium silicate to a previously prepared foundry mix containing the isocyanate and hydroxyl-containing material by using automatic blending equipment.

The metal silicates used in practicing the present invention are typically represented by the general formula $M_2O \cdot nSiO_2$ wherein M represents a metal ion and n is an integer (e.g. 2.5). The alkali metal silicates, especially sodium silicate, are preferred. Metal silicates of this type are well known and are commercially available. Mixtures of metal silicates can be used. Metal silicates are usually sold as powders (anhydrous or hydrated) or as aqueous solutions. Typically, the weight ratio of $M_2O:SiO_2$ in commercially available silicates is between 1:0.5 and 1:5, more usually from 1:1.5 to 1:4, e.g. from 1:2 to 1:3. The aqueous solutions usually contain between 25 and 90 weight percent water, e.g. 40-75 weight percent water. The balance, e.g. 45%, is metal silicate. Hydrated sodium silicate powders usually contain about 17.5 weight percent water, although other hydrates are known. For some reason, the advantages of the present invention have not been obtained to any significant extent when metal silicates are used under anhydrous conditions. It has been found that the ability to rapidly obtain stripping strength requires the critical presence of water in the system. Metal silicate powders can be used in conjunction with foundry mixes containing small amounts of water, e.g. an effective amount of up to 3% or more water based on the weight of the sand or other aggregate in the foundry mix. However, significantly better results are obtained if an aqueous solution of the metal silicate, e.g. aqueous sodium silicate, is employed. There is usually sufficient water in commercially-available metal silicate solutions to satisfy the requirements of this invention. The amount of metal silicate used in practicing this invention will be an effective amount ranging from more than mere incidental impurities up to as much as 5% based on the weight of aggregate (e.g. sand) in the foundry mix. Typically, the amount of metal silicate used will be from 0.1 to 3%, e.g. 0.2 to 1%, on the same basis.

As previously indicated, the known binder compositions which can be benefited by the practice of this invention are those which contain both a polyisocyanate and a hydroxyl-containing material which are co-reacted at or about the time of use in the presence of sand. Typically, the reactive ingredients of such binder compositions are sold, shipped, and stored in separate packages to avoid undesirable deterioration due to premature reaction between the components. Solvents, catalysts, various additives, and other known binders can optionally be used in conjunction with these essential ingredients, i.e. used with the polyisocyanate and hydroxyl-containing material.

- (2) Typically, cyclic and acyclic polyisocyanates containing from 2-5 isocyanate groups are employed. If desired, mixtures of polyisocyanates can be employed. Less prefer-

ably, isocyanate prepolymers formed by reacting excess polyisocyanate with a polyhydric alcohol (e.g. a prepolymer of toluene diisocyanate and ethylene glycol) can be employed. Suitable polyisocyanates include the aliphatic polyisocyanates such as hexamethylene diisocyanate; alicyclic polyisocyanates such as 4,4'-dicyclohexylmethane diisocyanate; and aromatic polyisocyanates such as 2,4- and 2,6- toluene diisocyanate, and diphenyl methane diisocyanate and the dimethyl derivative thereof. Further examples of suitable polyisocyanates are 1,5-naphthalene diisocyanate; triphenyl methane triisocyanate; xylylene diisocyanate and the methyl derivative thereof; polymethylene polyphenyl isocyanate; chlorophenylene-2,4-diisocyanate, and the like. All polyisocyanates do not serve with the same effectiveness. While the aforementioned polyisocyanates are, to a greater or lesser degree, effective in practicing the present invention, there are significant advantages associated with the use of cyclic polyisocyanates, especially the aromatic polyisocyanates, as contrasted to the aliphatic polyisocyanates. In general, aromatic polyisocyanates impart more rigidity to cores than do the aliphatic polyisocyanates. Diphenylmethane diisocyanate, triphenylmethane triisocyanate, and mixtures thereof are preferred because of their high degree of reactivity, desirable core forming properties, and low vapor pressure. The latter minimizes any possible toxicity problems.

The hydroxyl-containing material to be co-reacted with the isocyanate can be a polyhydric alcohol (e.g. pentaerythritol). High molecular weight hydroxyl-containing materials are preferred. Preferably, the hydroxyl-containing co-reactant will be an alkyd resin (e.g. an oil-modified alkyd resin), a hydroxyl-terminated polyester (e.g. alcoholysis products of fatty tri-glycerides), and polymers and copolymers containing reactive hydroxyl groups (e.g. hydroxy-alkyl acrylate copolymers). Hydroxyl-containing materials which can be hardened, at least in part, by air oxidation are particularly preferred. Thus, drying oil-modified alkyd resins, as well as various unsaturated fatty acid esters and unsaturated fatty acid modified polyesters are preferred. Oil-modified alkyd resins are the most preferred hydroxyl-containing reactants. With alkyd resins, especially the oil-modified alkyd resins, the hydroxyl value should be at least 25 and preferably above 50. The upper limit of hydroxyl value is only limited by practical considerations, e.g. viscosity. For most ordinary applications, oil-modified alkyd resins having hydroxyl values of from 50-250, e.g. 60-150, are desirable.

As indicated, the oil-modified alkyd resins are the preferred hydroxyl-containing reactants. In general, it is preferred to employ oil-modified alkyd resins which have been prepared from the following three classes of ingredients:

- (a) polyhydric alcohols having at least three hydroxyl groups, e.g. glycerol, pentaerythritol, trimethylol propane and the like. Pentaerythritol is preferred. Mixtures of polyhydric alcohols can be used. While glycols can be used, better results are obtained if such glycols are used in conjunction with the polyhydric alcohols (use a mixture of ethylene glycol and pentaerythritol). Ordinarily, only the polyhydric alcohols will be used.
- (b) polycarboxylic acids (or their anhydrides) such as maleic acid, fumaric acid, phthalic acid, phthalic anhydride, isophthalic acid, chlorogenic acid and the like. The various phthalic acids (particularly isophthalic acid and phthalic anhydride) are preferred. Mixtures of acids can be used.
- (c) oil such as soybean oil, linseed oil, cottonseed oil, castor and dehydrated castor oils, tall oil, tung oil, fish oil and the like. Mixtures of oils can be used. Linseed oil is preferred.

The more preferred oil-modified alkyd resins will contain at least 40 weight percent oil (based on the total weight of the alkyd resin formulation). More desirably, the alkyd resins will contain at least 50 weight percent oil on the

same basis (i.e. a "long oil alkyd"). It should be pointed out that oil-modified alkyd resins can also be prepared (as is known in the resin art) from fatty acids rather than the corresponding oils or glycerides.

The combination of isocyanate and hydroxyl-containing material can optionally be used in combination with other binder systems. The foundry mixes of this invention can optionally include other ingredients such as synthetic drying oils, natural drying oils, petroleum polymers, iron oxide, ground flax fibers, wood cereal, pitch, etc.

Catalysts are optionally and ordinarily used in conjunction with binder compositions containing both an isocyanate and a hydroxyl-containing material. The catalysts which are usually employed are those which accelerate the air oxidation of the hydroxyl-containing material, those which accelerate the reaction between the polyisocyanate and the hydroxyl-containing material, and those which do both. The amount of catalyst employed will be a catalytic amount, with the total amount of catalyst(s) usually ranging from 0.01-20%, based on the combined weight of the polyisocyanate and hydroxyl-containing material. More frequently, from 0.1-15%, e.g. 0.25-10% catalyst will be used, on the same basis. The choice of catalyst and the amount thereof will affect the curing rate of the system. Metal naphthenates (e.g. cobalt naphthenate) are effective catalysts for both the isocyanate/hydroxyl reaction and the air oxidation of the hydroxyl-containing reactant, the latter being their primary function. Sodium perborate can also be used to promote the oxygen cross-linking of the hydroxyl-containing material. Metal ion catalysts such as tetra(hydrocarbyl) tin catalysts are especially desired. Particularly preferred catalysts are the dibutyl tin di-(hydrocarbyl) catalysts. Dibutyl tin dilaurate is a very effective catalyst.

When combining the isocyanate and hydroxyl-containing material with sand (or some other aggregate) at or about the time a core is to be made, it is common to use from 5-150 parts by weight of polyisocyanate per 100 parts by weight of the hydroxyl-containing reactant. More frequently, from 5-90 parts, e.g. from 8-50 parts of polyisocyanate will be used on the same basis. With certain oil-modified alkyd resins it is common to use from 10-40 parts, e.g. 15-30 parts of polyisocyanate on the same basis.

The present invention will be further understood by reference to the following specific examples which include a preferred embodiment. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

A first mixture was prepared which contained 47 parts of oil-modified alkyd resin having a hydroxyl value above 50 (at 100% non-volatile) and containing over 50% oil, 29 parts of an air-hardenable petroleum polymer, 24 parts of mineral spirits, and 12 parts of a solution of cobalt naphthenate and dibutyl tin dilaurate. Next, a foundry mix was prepared by intimately mixing two parts of the first mixture with 100 parts of foundry sand and 0.4 part of an aromatic polyisocyanate (diphenylmethane diisocyanate sold as Mondur MR). This foundry mix was blended with 1 part of aqueous sodium silicate using automatic blending equipment set to deliver approximately 35 pounds of foundry sand mix per minute. The resulting sand mix was then used to form sand molds. The time required to achieve an acceptable level of stripping strength was about 8 minutes. Within 20 minutes, the sand mold had developed a good scratch hardness. This sand mold was then used to make aluminum castings. Casting results were excellent.

For comparative purposes, the procedure of Example 1 was repeated exactly except for the omission of the aqueous sodium silicate. When this foundry mix was used to form the same sand molds, the stripping time was 45 minutes.

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The aqueous sodium silicate used in Example 1 was Du Pont's #16. The aqueous solution contained approximately 45-49% sodium silicate having a weight ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ of from 1:2.3 to 1:2.5.

Example 2

The procedure of Example 1 was followed exactly, except for the ordinary variations inherent in the use of commercial automatic equipment. With the addition of aqueous sodium silicate (the same as Example 1), the stripping time was 3 minutes. Within 20 minutes after the mold had been stripped, a good scratch hardness had developed. Aluminum castings were made using the rapidly-cured mold and casting results were excellent.

For comparative purposes, this example was repeated exactly except for the omission of the sodium silicate. Once again, the stripping time without sodium silicate was approximately 45 minutes.

Example 3

A foundry sand mix is prepared by intimately mixing 100 parts of sand (Michigan Lake sand; AFS #55), 1.08 parts of an oil-modified alkyd resin having a hydroxyl number of about 105 (64.5% linseed oil, 14.4% pentaerythritol, and 21% isophthalic acid), 0.5 part of xylene, 0.42 part of a mixture of crude di- and triphenylmethane di- and triisocyanate (Mondur MR), 0.1 part of sodium perborate, and 0.08 part of a 6% solution of cobalt naphthenate. This foundry sand mix is then blended with 1.5 parts of a 35% aqueous solution of sodium silicate having a $\text{Na}_2\text{O}:\text{SiO}_2$ weight ratio of 1:2. This foundry sand mix is then used to prepare sand cores.

For comparative purposes, identical cores are prepared from a foundry mix differing from that of Example 3 only by the omission of the sodium silicate.

When the stripping times of the sand cores prepared from these two foundry sand mixes are compared, the stripping time accompanying the use of the first foundry sand mix (i.e. Example 3) will be significantly lower than that obtained with the second sand mix (i.e. the comparative example).

It is to be noted that the benefits accompanying the practice of the present invention do not require that the foundry mix be gassed after the addition of the sodium silicate nor does it require the use of any special catalyst or special decomposing agent.

Example 4

Results similar to those obtained in Examples 1-3 will be obtained when polymethylene polyphenyl isocyanate is used as the isocyanate component, a hydroxyl-containing ester is employed as the hydroxyl-containing material, and aqueous potassium silicate is used as the metal silicate. A suitable hydroxyl-containing ester can be prepared by reacting a mixture of 84 parts of linseed oil and 16 parts of pentaerythritol under alcoholysis conditions.

Example 5

Beneficial results similar to those obtained in Examples 1-4 will be obtained when toluene diisocyanate is used as the isocyanate component, when a hydroxyl-terminated polyester is employed as the hydroxyl-containing material, when the sand contains 1% water, and powdered sodium silicate containing about 17.5 weight percent water (as water of hydration) is used as the metal silicate.

From the foregoing description and examples, it will be appreciated that a novel procedure has been developed

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for increasing the speed with which an acceptable stripping strength can be obtained when using binder compositions containing both a polyisocyanate and a hydroxyl-containing material. Thus, by simply adding small amounts, e.g. 0.1 to 3% of alkali metal silicate (based on the weight of sand) to a foundry sand mix under hydrous conditions, rapidly curing sand cores and molds can be obtained. These results can be obtained without external gassing and without a requirement for the use of catalysts or decomposition agents which are specific to alkali metal silicates.

A further advantage to the inventive system is that one can reduce the amount of catalysts (e.g. a mixture of cobalt and lead naphthenates) ordinarily used with the isocyanate/hydroxyl binder and the system will still cure in an acceptable manner. Under the present economic conditions, this means a lower cost per ton of sand when the inventive system is used.

Although the present invention has been described with a certain degree of particularity, it will be realized that numerous minor changes and variations, falling within the spirit and scope of this invention, will become obvious to those skilled in the art. It is not intended that this invention be limited to any of the materials which have been specifically mentioned for the sake of illustration, nor by the specific proportions which have been given for the sake of illustration.

What is claimed is:

1. In a foundry process wherein cores are prepared from a foundry mix containing sand and a binding amount of a binder composition containing polyisocyanate and a hydroxyl-containing reactant, the improvement which comprises including a metal silicate in said foundry mix under hydrous conditions and thereafter preparing said cores.

2. The process of claim 1 wherein said metal silicate is sodium silicate and wherein the amount of sodium silicate used is from 0.1 to 3% based on the weight of sand.

3. The process of claim 2 wherein said sodium silicate is in the form of an aqueous sodium silicate solution containing from 10-95 weight percent water and having a weight ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ of from 1:2 to 1:3.

4. The process of claim 3 wherein said cores are prepared in the absence of gaseous catalysts and special decomposition agents for said sodium silicate.

5. The process of claim 3 wherein said binder composition comprises aromatic polyisocyanate, oil-modified alkyd resin having a hydroxyl value of at least 50, and catalyst.

6. The process of claim 5 wherein said catalyst is a mixture of cobalt naphthenate and dibutyl tin dilaurate.

7. The process of claim 3 wherein said sodium silicate is rapidly introduced into said foundry mix after said binder composition has been mixed with the sand and immediately prior to forming said cores.

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